

The x-ray analysis at high spectral resolution

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In x-ray emission spectroscopy, the spectral resolution or resolving power depends on the experimental broadening of the spectrometer and on the natural width of the lines. It is not possible to play on the second factor, which is given by nature. In the Johann-type spectrometers that are widely used for WDS microanalysis, the two main factors governing the instrumental broadening are the opening of the crystal and the diffraction pattern (width of the rocking curve) of the analyzing crystal. Generally in the commercial apparatus, the opening of the crystal is large to improve the intensity at the expense of the resolution. We show that it is possible to work at high spectral resolution by presenting :

- two examples of analysis performed with a spectrometer operating with a bent crystal having a small opening;
- one example obtained a plane spectrometer equipped with a multilayer grating having a narrow diffraction pattern.

Improving the resolution enables to be sensitive to the shape of the emission bands and then to distinguish different physico-chemical states of the emitting element. This is due to the fact that the valence states, whose distribution is described by the emission band, involve the less tightly bound electrons of the materials. As an example, the Al $K\beta$ emission band (3p-1s transition, around 1550 eV photon energy) is presented for the pure Al metal, Al in the TA6V alloy (a titanium-based alloy) and Al in alumina (Al_2O_3). The three chemical states of the aluminum atoms can be easily determined from the high-resolution analysis of the Al $K\beta$ emission band. This is used to study the superficial zone of a TA6V substrate *before* the deposition of an alumina film by PECVD. By using incident electrons having energies closer and closer to the Al 1s binding energy, a thinner and thinner zone is analyzed. Finally a superficial zone having a thickness of only a few nm is probed. In this zone the effect of the treatment suffered by the TA6V substrate is revealed by the fraction of Al atoms in the oxidized state with respect to those in the alloy state.

The second example deals with the study of aluminum impurities in a silica glass [1]. The goal is to determine if these impurities are in metallic form or not, to know if they can absorb the laser radiation at 355 nm from the Méga-Joule laser working at very high fluences ($>10 J/cm^2$). In this case the Al concentration is 50 ppm (in weight) and it is not possible to use the Al $K\beta$ emission band because it is too less intense. By using the Al $K\alpha$ atomic line (2p-1s transition, around 1487 eV photon energy) analyzed at high spectral resolution, it is possible to distinguish between the metallic and oxidized states of the Al atoms, as presented in the Figure 1. We show that the Al atoms are in octahedral environment, surrounded by six oxygen atoms, and then cannot be responsible of the damaging of the optics of the Méga-Joule laser.

The study of the 100-500 eV photon energy range is difficult with crystal-spectrometers because there exists no crystals having sufficiently large reticular distance. In this case, the diffractive optics are multilayer interferential mirrors (MIM). They consist of alternate layers of heavy (Mo, La, W, ...) and light (Si, C, B_4C , ...) materials. The sum of the thicknesses of the light and heavy layers (typically between 3 and 30 nm) plays the role of the reticular distance. The advantages of the MIM are that they can be optimized for a specific photon energy range and have large reflecting powers. However, their diffraction pattern is wide (some tenths of degrees) leading to poor resolution spectra. It is possible to improve the resolution by etching the MIM in order to produce multilayer gratings (MG). In this case, a decrease of the bandwidth by a factor 3 can be obtained at the expense of a relatively small decrease of the reflecting power. As an example, we present in the Figure 2 the spectrum emitted by a B_4C film deposited onto a silicon substrate, analyzed with a Mo/ B_4C MIM and with the MG obtained from this MIM [2]. The advantages of the MG over the MIM are clear :

- the improved resolution enables to separate the various emissions;
- the decrease of the total reflection angle leads to a small background towards the small Bragg angles and enables to lower the detection limit despite the loss of reflectivity.

These factors lead to an easiest quantitative analysis of the samples when using MG structures.

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[1] P. Jonnard, J.-P. Morreeuw, H. Bercegol, Eur. J. Phys. Appl. Phys 21 (2003) 147.

[2] R. Benbalagh et al., Nucl. Instrum. Meth. Phys. Res. A, submitted.

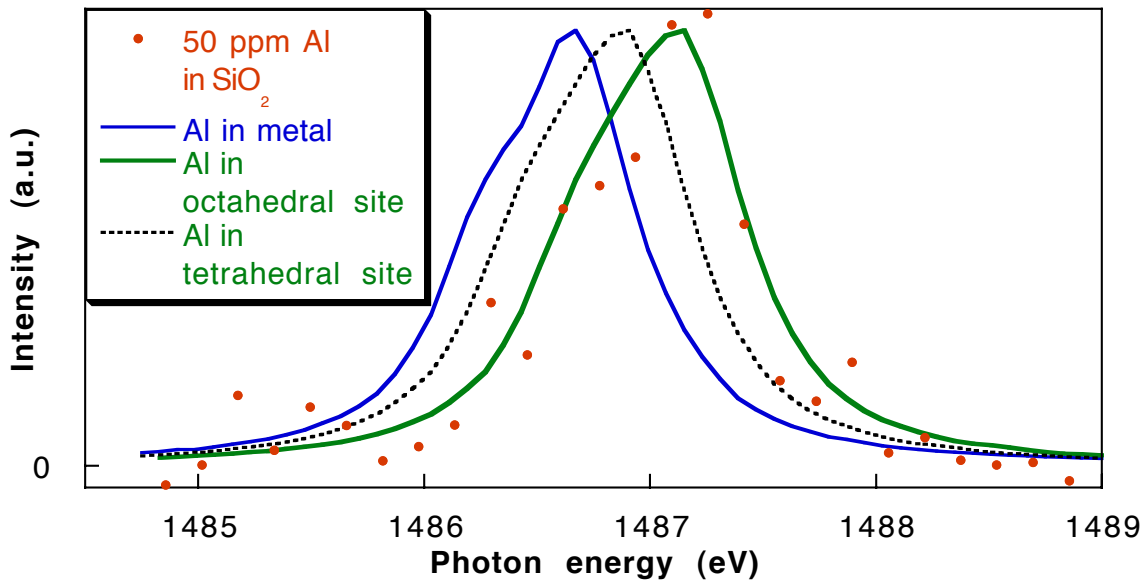


FIG 1 : High-resolution WDS spectrum of the Al K α emission from Al atoms in impurity inside a silica glass and in various environments.

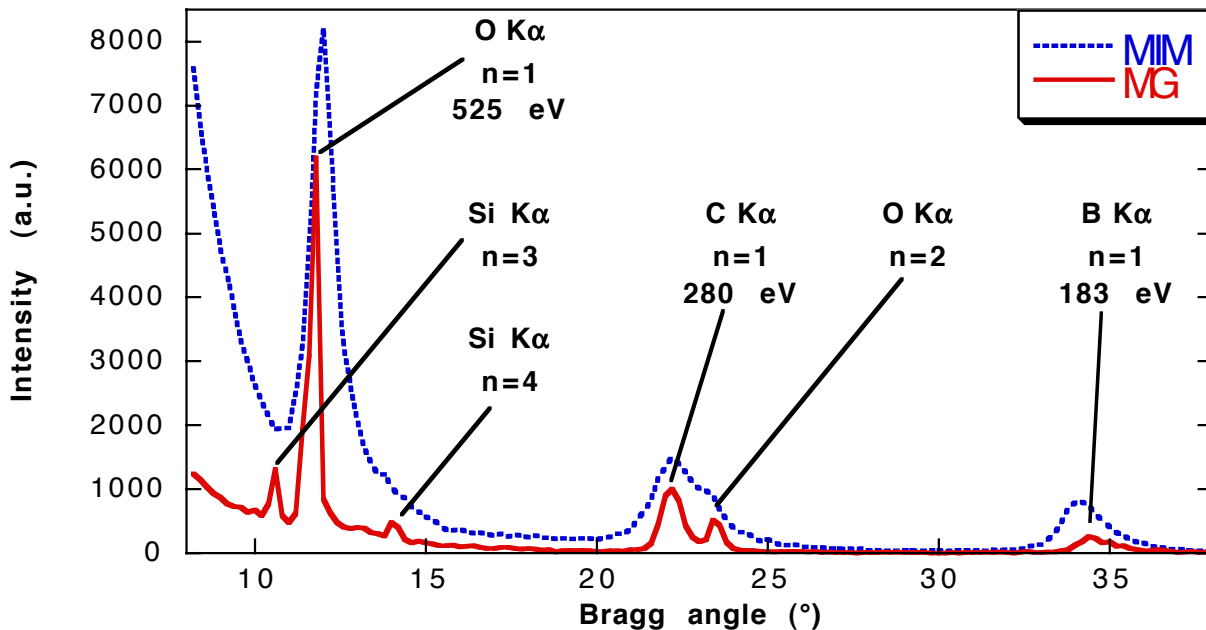


FIG 2 : WDS spectrum of a boron carbide film deposited onto a silicon substrate obtained with a Mo/B₄C MIM (dashed line) and with a “high resolution” MG (solid line).